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(54) Title: OLEFIN POLYMERIZATION CATALYSTS

(57) Abstract

An olefin polymerization catalyst system comprises a porous, particulate, cross-linked resinous styrene polymer substrate, and a metallocene and an aluminoxane disposed on the surface thereof.

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OLEFIN POLYMERIZATION CATALYSTS

This invention relates to olefin polymerization catalysts, and particularly to catalysts for the copolymerization of ethylene with a higher α -olefin to 5 produce a material referred to as linear low density polyethylene (LLDPE).

The polymerization of olefins, particularly ethylene, is well known and has been a widely practiced commercial art for many decades. Catalysts for such polymerization 10 are well known to include Ziegler type catalysts. In the Ziegler type catalyst field, the catalyst is usually made up of a transition metal compound and an alkyl aluminum, which is used as a co-catalyst, sometimes with a magnesium compound as well, usually on a suitable support.

15 In more recent times, it has been discovered that the copolymerization of ethylene and higher olefins can be catalyzed by special zirconium and/or hafnium compounds. These compounds, called metallocenes, have been proposed for use in this service in combination with aluminoxanes, 20 as co-catalysts, with both being deposited on a silica substrate.

The invention provides a novel olefin polymerization catalyst based on a metallocene catalyst and an aluminoxane co-catalyst on a specially designed organic polymeric 25 substrate. This substrate comprises a resinous, cross-linked, porous particulate material which is substantially insoluble in either the reactant monomers or the product polymers, or in common solvents which have been used as the polymerization media in slurry or solution based 30 polymerization processes. The substrate is also substantially insoluble in common solvents which are often used in the production of the polymerization catalyst.

Accordingly, the invention resides in its broadest aspect in a catalyst composition for copolymerizing 35 ethylene with an alpha olefin having 3 to 10 carbon atoms comprising a metallocene compound activated with an

aluminoxane and dispersed on the surface of a particulate porous organic substrate comprising a crosslinked polymerization product of styrene.

5 The chemically inert nature of the porous support results in a purely physical dispersion of the metallocene/aluminoxane deposited thereon to produce catalysts with higher activity and which yield polymers with narrower molecular weight distribution and higher molecular weight than silica-supported catalysts.

10 A catalyst prepared on the inert porous organic support of the invention does not require the use of external methylaluminoxane co-catalyst solutions. As such, it is ideally suited for gas phase polymerization reactors and does not require high aluminoxane/metallocene ratios.

15 The substrate of the catalyst of this invention is not a refractory material like silica, but rather is organic in nature. It obtains its insolubility in the solvents set forth above by reason of it having been made of a polymer which is substantially cross-linked. Furthermore, the 20 degree of cross-linking imparts porosity to the organic substrate, in contrast to nonporous (i.e., uncrosslinked) organic substrates.

25 The cross-linking of the polymeric substrate may be by reason of the inherent chemical composition of the polymer components, such as by the presence of at least some proportion of a monomer which has multiple functionality which reacts in the particle forming polymerization to create a cross-linked polymer particle during the initial polymerization reaction. A preferred example of such a 30 monomer is divinyl benzene. Alternatively, the cross-linking may be accomplished by means of a post polymerization cross-linking process, such as bombardment with high energy particles or peroxide treatment.

35 The preferred cross-linked porous polymer substrate is made by a suspension polymerization process by producing a copolymerization mixture comprising a water medium, as the

continuous phase, having added thereto suitable proportions of the desired monomers, e. g. styrene and divinyl benzene, suspending agent(s), polymerization initiator(s), porogen material(s), and any other component(s) which aid

5 suspension polymerization. The mixture is then subjected to conventional suspension polymerization conditions, whereby the co-monomers are polymerized and cross-linked; and the porogen-filled polymer particle products recovered. After harvesting the suspension polymer particles

10 containing the porogen, this component is suitably removed, usually by the use of solvents or steam. The thus made particles are then dried to form free-flowing, porous particles in which the pores are substantially empty.

Where the polymer particle is to be cross-linked after

15 it has been made, as compared to cross-linking the polymer during the initial polymerization, the initial suspension polymerization is carried out in the manner set forth above up to the stage where the porous resinous particles, containing the porogen, are recovered. The post cross-

20 linking process should then be carried out while the porogen is still in place, and, after cross-linking has been completed, the porogen is suitably removed in the same manner as aforesaid.

Typical porogen materials include those materials

25 which are substantially inert with respect to the final polymer particles, which will be incorporated within the polymer particles, but which will not be chemically bound to the particles. These porogens are exemplified by substantially non-functional materials which are

30 substantially liquid under the conditions of polymerization and recovery of the polymer particles, such as for example mineral oil, heptane and toluene. The pore size, pore size distribution, and the surface area of the resulting polymer particles are, to a great extent, a function of the

35 particular porogen which is employed, the amount of porogen

present during polymer particle formation, and the degree of cross-linking in the polymer.

Reference is here made to the following journal articles: "Macroreticular Resins. III. Formation of 5 Macroreticular Styrene-Divinyl Benzene Copolymers", K. A. Kun and R. Kunin, *J. Polymer Science: Part A-1*, Vol. 6, 2689-2846 (1968); and "Styrene-Divinyl Benzene Copolymers. Construction of Porosity in Styrene-Divinyl Benzene Matrices", W. L. Sederel and G. J. DeJong, *J. Applied 10 Polymer Science*, Vol. 17, 2835-2846 (1973).

These articles describe a suitable, and even a preferred, manner of making the cross-linked, porous, resinous substrates of the catalyst systems of this invention.

15 The resinous, cross-linked, porous particulate substrate for use in conjunction with a metallocene olefin polymerization catalyst suitably comprises a polymer which is not only cross-linked, but is not readily susceptible to deterioration under the conditions under which the catalyst 20 is applied thereto and/or the conditions of the use of the supported catalyst in olefin polymerization. Addition polymers are most well suited to use in this service. Particularly the polymerization products of vinyl addition reactions, preferably of aliphatic and/or aromatic vinyl 25 hydrocarbons, are well suited to this use. These include poly (aliphatic) vinyl polymers, poly (aromatic) vinyl polymers, poly divinyl polymers, copolymers of these monomer categories, and the like. Hydrocarbonaceous polymers which are cross-linked or cross-linkable are the 30 preferred composition of the substrate particles of this invention.

Cross-linked aromatic addition polymers are the 35 preferred hydrocarbonaceous polymers for use in this invention. The most preferred resinous materials are styrene-divinyl benzene co-polymers. When this polymer system is used, the pore size of the resulting polymer

particles is not only a function of the particular porogen which has been selected, but is also a function of the proportion of divinyl benzene which is employed. In this regard, it should be noted that commercial divinyl benzene 5 is usually a mixture of isomers and saturated ethylene derivatives. It most commonly contains about 50% of the desired para isomers. When considering the proportion of the copolymer which is to be made up of divinyl benzene, it is usually only the para isomer which engages in the 10 polymerization, and therefore, only the amount of this isomer should be considered in determining the proportions of this monomer.

In one preferred aspect of this invention, in which the porous substrate has substantially no surface activity, 15 the proportion of styrene monomers comprises up to 94 weight per cent and the remainder (considering only the para isomer) divinyl benzene. This is sufficient to make a cross-linked polymer product. The preferred proportion of styrene monomer in this system is 60 to 80 weight per cent.

20 In addition to the monomer or monomers which are needed to form the fundamental resinous particle of the support, it is also possible to provide additional co-monomers in the co-polymerization monomer mixture. These additional co-monomers may satisfy and provide certain 25 additional functions as needed and they then may become incorporated within the resinous polymer product and exert an effect on the operation of the catalyst.

In one such embodiment, the additional monomers containing reactive groups which are not substantially 30 reactive with the strictly hydrocarbon basic monomers, are included in the monomer mixture which is co-polymerized to produce the desired substrate particle, and are copolymerized along with the basic monomers to form the catalyst substrate particles. These pendant additional 35 monomers remain as unreacted functional groups after the

formation of the cross-linked resinous particles and are desirably co-polymerized directly into the cross-linked co-polymer in a manner such that their "non-reactive" functional groups remain active on the surface of the 5 resultant resinous substrate particles. In this condition, they are readily available for further reaction after the crosslinked resinous catalyst substrate particle has been formed.

The additional functional co-monomers preferably have 10 the same fundamental structure and chemistry as the co-monomers which are being co-polymerized to form the basic porous particle of this invention. Thus, in the situation where aromatic monomers, like styrene and divinyl benzene, are the basic polymerization building blocks, the added 15 functional co-monomer should also preferably have a styrene, or at least an aromatic type, core structure.

Moreover, it is important that the functional group of the additional monomer is substantially inert during the polymerization of the basic monomers. Thus, if the cross-linked polymer which will form the fundamental particle 20 substrate for use in this invention is an olefin addition polymer, the added functional group should be one which does not readily react with olefinic unsaturation under the polymerization conditions. On the other hand, if the fundamental polymer of the particulate substrate is a 25 condensation polymer, such as a polyester or a polyamide, the additional functional group may be an olefinic unsaturation, provided that it does not react to any appreciable extent in the polymerization condensation reaction. In addition, the polymerization conditions 30 should be taken into account when selecting the monomers being reacted so as to insure that only those desired functional substituents react in the polymerization, only those desired portions of the polymer react in the cross-linking, and those desired functional groups which need to 35

be retained do not react at all in the basic process of producing the crosslinked resinous porous particle.

Suitable additional monomers for use in this embodiment include acrylic and methacrylic acids and esters, vinyl ethers, such as methyl vinyl ether, vinyl esters, such as vinyl acetate, vinyl halides, such as vinyl chloride, acrylonitriles, alkylene glycol di-acrylates and methacrylates, such as ethylene and propylene glycol di-acrylates and methacrylates, hydroxy terminated unsaturated acids and esters, such as ω hydroxy acrylic acid and esters thereof, halo substituted aromatic olefins, such as chlorostyrene or chloro-divinyl benzene, hydroxy substituted styrene, p-acetoxy styrene or divinyl benzene, vinyl toluene, vinyl pyridine, vinyl benzyl halides, such as vinyl, benzyl chloride, and the like, are quite useful. It is within the scope of this invention to use between 1 and 30 weight percent of one or more additional monomers containing at least one pendant functional group in admixture with the basic monomer(s). In one aspect of this invention, where the basic monomers are styrene and divinyl benzene, this proportion of added monomer is copolymerized with a mixture comprising up to about 94 % styrene and the remainder, that is at least about 6 %, divinyl benzene.

The use of the additional functional monomer provides another degree of freedom in controlling the properties of the ethylene polymerization products produced using catalysts of the metallocene/aluminoxane/resinous substrate type. Thus, where the pendant functional group is an acetoxy group; where the catalyst comprises a zirconocene, an aluminoxane, and an aluminum hydrocarbyl on a crosslinked, porous, resinous styrene-divinyl benzene substrate; where the catalyst has been made in substantially the same way and with the same proportions of constituents; and where the ethylene polymerization has been carried out under the substantially the same conditions, the polymer product produced can have a melt

index about three (3) orders of magnitude higher than where the catalyst substrate does not have a functional monomer copolymerized therewith.

5 In one preferred embodiment of the invention, in which the resinous substrate has no surface functionality, the substrate is a cross-linked styrene-divinyl benzene co-polymer comprising about 80 weight percent styrene and 20 weight per cent divinyl benzene.

10 In an alternative preferred formulation, in which the substrate has surface functionality, the divinyl benzene comprises about 30 % by weight of the crosslinked resinous substrate, the styrene comprises about 55 %, and functional added monomer is p-acetoxy styrene which comprises about 15 % thereof.

15 The porosity of the styrene polymer support particles of the invention is preferably controlled so that the pore size is between 100 and 1050 Angstrom. In fact it has been found that in the catalyst system of this invention, if all of the polymerization conditions are kept relatively 20 constant, the molecular weight of the product co-polymer decreases as a function of decreasing average pore diameter. Therefore, in order to use the catalyst system of this invention to produce relatively low molecular weight ethylene co-polymerization products, that is 25 products having melt indices of at least about 10, preferably at least about 15, it is preferred that the average pore diameter of the resinous substrate is not more than 300 Å, preferably not more than 200 Å. The particle size of the carrier substrate preferably ranges from 10 to 30 100 microns, more preferably 30 to 50 microns.

The aluminoxanes used in the catalyst of the invention comprise oligomeric linear and/or cyclic alkylaluminoxanes represented by the formula:

R-(Al(R)-O)_n-AlR₂ for oligomeric, linear aluminoxanes and (-Al(R)-O-)_m for oligomeric cyclic aluminoxanes wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group, preferably a C₁-C₃ alkyl, and most preferably methyl. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene. The aluminoxane is preferably present in an amount to provide 0.1 to 20 mmol Al/gram of support.

The metallocene compound used in the catalyst of the invention has the formula $Cp_mMA_nB_p$ in which Cp is an unsubstituted or substituted cyclopentadienyl group, M is zirconium or hafnium, preferably zirconium, and A and B belong to the group including a halogen atom, hydrogen or an alkyl group in the formula, $m+n+p =$ the balance of M, m is at least one, preferably 2, and each of n and p may be 0, 1, 2 or 3. In the above formula of the metallocene compound, where Cp is a substituted cyclopentadienyl group, the or each substituent is preferably a straight or branched chain C_1-C_6 alkyl group. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when m in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as $-CH_2-$, $-CH_2-CH_2-$, $-CR'R''-$ and $-CR'R''-CR'R''-$ where R' and R'' are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$ and similar bridge groups. If the substituents A and B in the above formula of the metallocene compound are alkyl groups, they are preferably straight-chain or branched C_1-C_6 alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and

5 bis(indenyl)metal dihalides wherein the metal is zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C₁-C₆ alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl) zirconium dichloride,

10 bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl) hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride,

15 bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride,

20 bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride. The metallocene compounds can be used as solutions in aromatic hydrocarbons.

The preferred metallocene is cyclopentadienyl zirconium chloride in a preferred proportion of 0.025 to 0.65 mmol/gram of support.

The catalyst conveniently also comprises a hydrocarbyl aluminum compound, preferably an alkyl aluminum, wherein the alkyl group has up to 8 carbon atoms, preferably up to 30 6 carbon atoms, and more preferably a branched alkyl group such as isoprenyl or isobutyl, most preferably isoprenyl. The hydrocarbyl aluminum compound is preferably present in an amount to provide 0.1 to 6 mm Al/gram of support.

To produce the catalyst of the invention, the 35 metallocene and aluminoxanes are conveniently dissolved in

a solvent, in which the substrate particles are insoluble, such as toluene, and the solution is then introduced into contact with the empty, porous cross-linked polymer particles and absorbed onto the surface thereof. Catalyst 5 preparation is undertaken under anhydrous conditions and in the absence of oxygen. Solvent may be removed from the impregnated pores of the carrier material by heating and/or under a vacuum or purged with heating in an inert gas, such as nitrogen. Upon drying, the thus produced catalysts are 10 then ready for use in a polymerization process.

Another advantage of this invention is the preparation of metallocene/aluminoxane catalysts on inert porous substrates that do not require the presence of external methylaluminoxane co-catalyst. This imparts several 15 advantages to this catalyst system. Nonrequisite use of methylaluminoxane co-catalyst makes these catalysts ideally suited for gas phase polymerizations, since methylaluminoxane co-catalyst solutions have resulted in serious process problems in fluid-bed (gas phase) reactors. 20 Another advantage is more prudent use of expensive methylaluminoxane since much lower methylaluminoxane to metallocene ratios are required for the catalyst system of the invention.

The invention will now be more particularly described 25 with reference to the following examples in which all parts and percentages are by weight unless specifically stated to be on some other basis.

EXAMPLE 1

2.5 grams of a cross-linked co-polymer of 80% styrene 30 and 20% divinyl benzene, which had an average pore diameter of 1050 Angstroms, was dried under vacuum at 100°C for 12 hours. To the dried co-polymer beads, 50 cc of toluene was added and the slurry mixture heated to 70°C with stirring. Then 2.1 cc of a 25% solution of isoprenyl aluminum in 35 hexane was added. After stirring for 10 minutes, 1.7 cc of

a 12% solution (5.8 wt% Al) of methylaluminoxane in toluene was added. After stirring for 30 minutes, a solution of 0.05 g Cp_2ZrCl_2 , dissolved in 10 cc toluene was added. The solvent was then removed by nitrogen purging at 80°C for 5 several hours until dry. The resulting catalyst was composed of 0.068 mmol of bis(cyclopentadienyl) zirconium dichloride/gram of support; 1.3 mmol, based on aluminum, of methylaluminoxane/gram of support; and 1.0 mmol, based on aluminum, of isoprenyl aluminum/gram of support.

10 Ethylene Polymerization

Polymerization was performed in a 4 liter slurry autoclave reactor equipped with propeller stirrer, external heating jacket for temperature control, a catalyst, and co-catalyst inlet and a regulated supply of dry nitrogen, 15 ethylene, and 1-hexene. The internal walls of the reactor were dried by baking at 85°C for one hour under a slow nitrogen stream. After cooling to ambient temperature, 1.45 liters of dry hexane and 0.25 liter of 1-hexene were delivered to the reactor under a steady nitrogen stream. 20 Then 2.0 cc of a 12% solution (5.8 wt.% Al) of methylaluminoxane in toluene was injected into the reactor. The reactor was heated to 85°C with stirring at 900 rpm, filled with ethylene until a total pressure of 1135 kPa (150 psig) was obtained and then 0.11 g of the catalyst was injected 25 into the reactor using a hexane filled bomb containing 1480 kPa (200 psig) ethylene. The polymerization reaction was allowed to proceed for 60 minutes. A yield of 112 grams of co-polymer product was obtained. The polymer had a melt index (I_2) of 1.9 g/10 min. The productivity of the 30 catalyst was 810 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR= I_{21}/I_2) of the co-polymer was 19.

COMPARATIVE EXAMPLE 1

A solid catalyst was prepared in the same way as in Example 1 except Davison 955 silica (calcined for 12 hours

5 at 600°C) instead of the cross-linked polymer was used as the solid support. The silica support had an average pore diameter of 200 Angstroms. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I₂) of 34 g/10 min. The productivity of the catalyst was 510 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR=I₁,I₂) of the co-polymer was 17.

COMPARATIVE EXAMPLE 2

10 A solid catalyst was prepared in the same way as in Example 1 except nonporous spherical (1% cross-linked) polystyrene (#200-#400, a product of Eastman Kodak Co.) was used as the solid support. The resulting catalyst was highly agglomerated and could not be fed into the reactor.

EXAMPLE 2

15 A solid catalyst was prepared in the same way as in Example 1 except the cross-linked polymer used as the solid support had an average pore diameter of 110 Angstroms. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I₂) of 19 g/10 min. The 20 productivity of the catalyst was 1240 g/g catalyst/hr/100 psi ethylene.

EXAMPLE 3

25 A solid catalyst was prepared in the same way as in Example 1 except the cross-linked polymer used as the solid support had an average pore diameter of 260 Angstroms. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I₂) of 16 g/10 min. The productivity of the catalyst was 1380 g/g catalyst/hr/100 psi ethylene.

30

EXAMPLE 4

One gram of a cross-linked polymer of 80% styrene and 20% divinyl benzene was dried under vacuum at 100°C for 12

hours. The dried co-polymer was slurried in 10 ml heptane, and 1.3 ml of 15% trimethylaluminum in heptane was added. After stirring for one hour at 70°C, the solvent was removed by nitrogen purging at 70°C for one hour. The 5 trimethylaluminum-treated beads were reslurried in 10 ml toluene, to which a solution of 0.03 gram of bis(n-butylcyclopentadienyl) zirconium dichloride in 2.7 ml of 15.8 wt.% Al methylaluminoxane in toluene was added with stirring at 70°C for 30 minutes. Solvent was removed by 10 nitrogen purging at 70°C for 1 hour followed by vacuum drying at 70°C for 2 hours. The resulting catalyst was composed of 0.075 mmol of bis(cyclopentadienyl) zirconium dichloride/gram of support; 15.0 mmol, based on aluminum, of methylaluminoxane/gram of support; 1.9 mmol, based on 15 aluminum, of trimethylaluminum/gram of support.

Ethylene Polymerization

Polymerization was performed in a 4 liter slurry autoclave reactor equipped with propeller stirrer, external heating jacket for temperature control, a catalyst, and co-catalyst inlet and a regulated supply of dry nitrogen, 20 ethylene, and 1-hexene. The internal walls of the reactor were dried by baking at 85°C for one hour under a slow nitrogen stream. After cooling to ambient temperature, 1.50 liters of dry heptane and 0.35 liter of 1-hexene were 25 delivered to the reactor under a steady nitrogen stream. Then 1.7 cc of a 15% solution of trimethylaluminum in heptane was injected into the reactor. The reactor was heated to 80°C with stirring at 900 rpm, filled with ethylene until a total pressure of 1340 kPa (180 psig) was 30 obtained, and then 0.19 g of the catalyst was injected into the reactor using a heptane filled bomb containing 1620 kPa (220 psig) ethylene. The polymerization reaction was allowed to proceed for 45 minutes. A yield of 238 grams of 35 co-polymer product was obtained. The polymer had a melt index (I_2) of 0.52 g/10 min. The productivity of the

catalyst was 920 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR=I₂₁/I₂) of the co-polymer was 17.

COMPARATIVE EXAMPLE 3

A solid catalyst was prepared in the same way as in Example 4 except PQ 988 silica (calcined for 12 hours at 600°C) instead of the cross-linked polymer used as the solid support. Polymerization was carried out as in Example 4. The co-polymer product had a melt index (I₂) of 0.38 g/10 min. The productivity of the catalyst was 310 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR=I₂₁/I₂) of the co-polymer was 22.

COMPARATIVE EXAMPLE 4

A solid catalyst was prepared in the same way as in Example 4 except nonporous spherical (1% cross-linked) polystyrene (#200-#400, a product of Eastman Kodak Co.) was used as the solid support. The resulting catalyst was highly agglomerated and could not be fed into the reactor.

EXAMPLE 5

Five grams of a cross-linked polymer of 55% styrene, 20 30% divinyl benzene, and 15% p-acetoxy styrene, where the acetoxy groups of the terpolymer were hydrolyzed to hydroxy groups with hydrazine, were dried under vacuum at 110°C for 12 hours. To the dried copolymer beads, 50 cc of toluene was added and the slurry mixture heated to 70°C with stirring. Then 4.2 cc of a 25% solution of isoprenyl aluminum in hexane was added. After stirring for 10 minutes, 3.4 cc of a 12% solution (5.8 wt% Al) of methylaluminoxane in toluene was added. After stirring for 30 minutes, a solution of 0.10 g Cp₂ZrCl₂ dissolved in 10 cc 25 toluene was added. The solvent was then removed by nitrogen purging at 80°C for several hours until dry. The resulting catalyst was composed of 0.068 mmol of bis(cyclopentadienyl)zirconium dichloride/gram of support;

1.3 mmol, based on aluminum, of methylaluminoxane/gram of support; and 1.0 mmol, based on aluminum, of isoprenyl aluminum/gram of support.

Ethylene Polymerization

5 Polymerization was performed as in Example 1 to produce after 60 minutes a yield of 97 grams of co-polymer product was obtained. The polymer had a melt index (I_2) of 430 g/10 min. The productivity of the catalyst was 490 g/g catalyst/hr/100 psi ethylene.

10 COMPARATIVE EXAMPLE 5

A solid catalyst was prepared in the same way as in Example 5 except Davison 955 silica (calcined overnight at 600°C) instead of the cross-linked polymer was used as the solid support. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I_2) of 34 g/10 min. The productivity of the catalyst was 500 g/g catalyst/hr/100 psi ethylene. The melt flow ratio ($MFR=I_2/I_1$) of the co-polymer was 17.

COMPARATIVE EXAMPLE 6

20 A solid catalyst was prepared in the same way as in Example 5 except the cross-linked polymer used as the solid support was composed of a copolymer of 80% styrene and 20% divinyl benzene. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I_2) of 1.9 g/10 min. The productivity of the catalyst was 810 g/g catalyst/hr/100 psi ethylene.

COMPARATIVE EXAMPLE 7

30 A solid catalyst was prepared in the same way as in Example 5 except spherical non-porous (1% cross-linked) polystyrene (#200-#400, a product of Eastman Kodak Co.) was used as the solid support. The resulting catalyst was highly agglomerated and could not be fed into the reactor.

EXAMPLE 6

A solid catalyst was prepared in the same way as in Example 5 except the cross-linked polymer used as the solid support was composed of a terpolymer of 55% styrene, 30% divinyl benzene, and 15% p-acetoxy styrene. Polymerization was carried out as in Example 1. The co-polymer product had a melt index (I_2) of 1500 g/10 min. The productivity of the catalyst was 560 g/g catalyst/hr/100 psi ethylene.

EXAMPLE 7

One gram of a cross-linked polymer of 55% styrene, 30% divinyl benzene, and 15% p-acetoxy styrene, where the acetoxy groups of the terpolymer were hydrolyzed to hydroxy groups with hydrazine, were dried under vacuum at 110°C for 12 hours. The dried copolymer was slurried in about 20 ml heptane and 1.4 ml of 15% trimethylaluminum in heptane was added. After stirring for one hour at 70°C, the solvent was removed by nitrogen purging at 70°C for one hour. The trimethylaluminum-treated beads were reslurried in about 20 ml toluene, to which a solution of 0.030 gram of bis(*n*-butylcyclopentadienyl)zirconium dichloride in 3.2 ml of 13.7 wt% Al methylaluminoxane in toluene was added with stirring at 70°C for 30 minutes. Solvent was removed by nitrogen purging at 70°C for 2 hours, after which free flowing beads were obtained. The resulting catalyst was composed of 0.075 mmol of bis(cyclopentadienyl)zirconium dichloride/gram of support; 15.0 mmol based on aluminum, of methylaluminoxane/gram of support; 1.9 mmol, based on aluminum, of trimethyl-aluminum/gram of support.

Ethylene Polymerization

Polymerization was performed in a 4 liter slurry autoclave reactor equipped with propeller stirrer, external heating jacket for temperature control, a catalyst and co-catalyst inlet and a regulated supply of dry nitrogen, ethylene, and 1-hexene. The internal walls of the reactor

were dried by baking at 85°C for one hour under a slow nitrogen stream. After cooling to ambient temperature, 1.50 liters of dry hexane and 0.35 liter of 1-hexene were delivered to the reactor under a steady nitrogen stream.

5 Then 1.7 cc of 15% solution of trimethyl aluminum in heptane was injected into the reactor. The reactor was heated to 80°C with stirring at 900 rpm, filled with ethylene until a total pressure of 1340 kPa (180 psig) was obtained, and then 0.12 g of the catalyst injected into the

10 reactor using a hexane filled bomb containing 1620 kPa (220 psig) ethylene. The polymerization reaction was allowed to proceed for 60 minutes. A yield of 199 grams of co-polymer product was obtained. The polymer had a melt index (I_2) of 1.0 g/10 min. The productivity of the catalyst was 1000 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR= $I_{21}I_2$) of the co-polymer product was 15.

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COMPARATIVE EXAMPLE 8

A solid catalyst was prepared in the same way as in Example 7 except PQ 988 silica (calcined for 12 hours at 600°C) instead of the cross-linked polymer used as the solid support. Polymerization was carried out as in Example 7. The co-polymer product had a melt index (I_2) of 0.38 g/10 min. The productivity of the catalyst was 310 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR= $I_{21}I_2$) of the co-polymer was 22.

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COMPARATIVE EXAMPLE 9

A solid catalyst was prepared in the same way as in Example 7 except a copolymer of 80% styrene and 20% divinyl benzene was used as the solid support. Polymerization was carried out as in Example 7. The co-polymer product had a melt index (I_2) of 0.52 g/10 min. The productivity of the catalyst was 920 g/g catalyst/hr/100 psi ethylene. The melt flow ratio (MFR= $I_{21}I_2$) of the co-polymer was 17.

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COMPARATIVE EXAMPLE 10

A solid catalyst was prepared in the same way as in Example 7 except nonporous 1% cross-linked polystyrene (#200-#400, a product of Eastman Kodak Co.) was used as the 5 solid support. The resulting catalyst was highly agglomerated and could not be fed into the reactor.

CLAIMS:

1. A catalyst composition for copolymerizing ethylene with an alpha olefin having 3 to 10 carbon atoms comprising a metallocene compound activated with an aluminoxane and dispersed on the surface of a particulate porous organic substrate comprising a crosslinked polymerization product of styrene.
5
2. A catalyst composition as claimed in claim 1 wherein the particles of the crosslinked styrene polymer have pores with an average pore diameter of 110 to 1050 Angstroms.
10
3. A catalyst composition as claimed in claim 1 or claim 2 wherein said substrate comprises a crosslinked copolymerization product of styrene and a further vinyl monomer.
15
4. A catalyst composition as claimed in claim 3 wherein said further vinyl monomer is divinylbenzene.
5. A catalyst composition as claimed in claim 1 wherein said copolymer comprises at least 6 weight per cent of divinylbenzene based on the total weight of styrene and divinylbenzene in the copolymer.
20
6. A catalyst composition as claimed in any one of claims 3 to 5 wherein said copolymer comprises an additional monomer which provides surface functionality on the substrate particles.
25

7. A catalyst composition as claimed in claim 6 wherein said additional monomer is selected from acrylic acid, methacrylic acid, vinyl acetate, methyl vinyl ether, vinyl chloride, p-acetoxy styrene, chloro styrene, chloro divinyl benzene, vinyl toluene, ethylene glycol diacrylate, ethylene glycol dimethacrylate, vinyl benzyl chloride, and vinyl pyridine.
- 5 8. A catalyst composition as claimed in claim 6 wherein said additional monomer is p-acetoxy styrene and 10 comprises 1 to 30 weight percent of the mixture used to form the copolymerization product.
9. A catalyst composition as claimed in any preceding claim wherein said aluminoxane is methylaluminoxane.
10. A catalyst composition as claimed in any preceding 15 claim wherein said metallocene compound is bis cyclopentadienyl zirconium dichloride.
11. Use of a catalyst composition as claimed in any preceding claim in the copolymerization of ethylene with an alpha olefin having 3 to 10 carbon atoms.

INTERNATIONAL SEARCH REPORT

In. national application No.
PCT/US95/02174

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 4/02; B01J 31/06
US CL :502/109, 159; 526/160

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/109, 159; 526/160

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,118,648 (FURTEK ET AL.) 02 June 1992, column 3, lines 27-36 and 62-65; column 4, lines 13-18.	3-5
X	US, A, 4,921,825 (KIOKA ET AL.) 01 May 1990, column 7, lines 1-8 and 45-49; column 12, lines 62-65; example 16.	1-2
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Y	US, A, 4,900,706 (SASAKI ET AL.) 13 February 1990, column 8, lines 15-45.	3-5
Y	US, A, 4,808,561 (WELBORN, JR.) 28 February 1989, column 1, lines 28-37; column 2, lines 32-44.	3-5

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"B"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
23 MARCH 1995	04 MAY 1995

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer <i>DAVID WU</i> DAVID WU
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02174

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 6-11 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.